

VERY HIGH FREQUENCY EPR OF SULFUR COMPOUNDS IN COAL

R. B. Clarkson, R. L. Belford, P. Ceroke, W. Wang, W. Shi, K. Motsegood,
A. Smirnov, T. Smirnova, M. J. Nilges
Illinois EPR Research Center
University of Illinois, Urbana, IL 61801

Keywords: Aromatic sulfur, EPR, quantitative measurement

INTRODUCTION

The overall goal of our work during the last five years has been the non-destructive elucidation of molecular structure in coal and coal-derived materials [1]. Special emphasis has been placed on determining the concentration and molecular forms of organic sulfur in coal. Our approach has been to use the naturally occurring unpaired electrons in coal as reporters of their environment, making use of electron magnetic resonance (EMR) spectroscopy to develop a detailed picture of the types and arrangements of atoms "seen" by the electrons. During this period, we constructed the first 95 GHz (W-band) EMR spectrometer in the USA (and the second in the world). With this advanced spectrometer, we were the first to discover that the aromatic sulfur in coal produced a unique EMR signature. Extensive experimental and theoretical work on model aromatic sulfur compounds in the thiophene series (thiophene, benzothiophene, dibenzothiophene, etc.) has enabled us to develop a detailed understanding of the relationships between the molecular and electronic structure of these compounds and their EMR spectra. This new basic scientific knowledge in turn allowed us accurately to analyze the W-band EMR spectra from coal, desulfurized coal, and a variety of coal derived materials. We developed an automated computer program (based on spin quantum mechanics) which can analyze the EMR spectra and which reports the aromatic sulfur content of the coal as well as key spectral parameters. This analysis method has been tested on coal blends of known sulfur content as well as on a variety of coals from the IBCSP and elsewhere. The precision of the method is conservatively $\pm 0.1\%$ of the aromatic sulfur in the sample. Identical samples measured both by EMR and XANES gave nearly identical results. The EMR technique has the twin advantages of simplicity and absolute concentration readout; an analysis takes less than five minutes to perform. Applications of the EMR technique include the determination of aromatic sulfur in coal, evaluation of the effectiveness of desulfurization technologies, and the evaluation of the effects of desulfurization on the rest of the molecular forms in coal.

EXPERIMENTAL PROCEDURES

A. Coal Sample Preparation

Significant progress has been made in the development of a standard protocol for coal sample preparation. Following the same protocol for all the samples allows the direct comparison of results from various types of coals. The development of a standard method also allows the calibration of the precision of the techniques and calculation of error limits. The techniques developed must allow for the sensitivity of coal samples to oxygen.

Since the EPR lineshape changes when samples are exposed to oxygen, preparation of coal samples for EPR analysis is done in a nitrogen atmosphere glove bag. All the necessary items needed for coal sample preparation, including the coal samples are exposed to nitrogen environment for two to three days. The oxygen concentration inside the bag is monitored continuously by keeping an oxygen sensitive electrode in the glove bag. The oxygen meter used is manufactured by "Yellow Springs Instrument Company" Yellow Springs, Ohio. The electrode utilizes a membrane with a KCl solution on the inside. The membrane must be kept wet so the electrode is stored in a beaker of distilled water. This meter gives oxygen concentration directly in ppm. EPR sample tubes are prepared at the oxygen level $\sim 4-6$ ppm. The EPR sample tubes (.7 mm O.D. quartz tube) are sealed at one end before being placed inside the glovebag. After the tubes are filled, a high quality vacuum grease is applied on the open end and tubes were carefully transferred in small labeled plastic vials. The vials are removed from the glovebag only when EPR spectroscopy is done.

B. W- Band EPR Spectroscopy

The key to our work plan is the W-band spectrometer. This unique instrument has been built over the last three years, and now incorporates several important technical innovations that make it well-suited for the present research work [2]. All spectroscopy at W-band (ca. 95 GHz) is done on the instrument constructed in our laboratory. Routine spectra were taken under nitrogen gas flow to avoid any possible oxygen sensitive changes. Lower power (15 db) is used to avoid saturation effects. Different modulation amplitudes were tried and finally a best compromise was achieved between the S/N ratio and the resolution of the spectrum. Data is acquired by a computer, which also controls the magnetic field sweep of the experiment.

C. Model Compounds

A 1000:1 mole ratio mixture of powdered boric acid (Aldrich) and the selected member of the thiophene series (thiophene, benzothiophene, dibenzothiophene, benznaphthothiophene, dinaphthothiophene, thianthrene) is heated to the melting point of boric acid (190°C). The molten mass is vortexed to maximize the dispersion of the selected thiophene in the molten solution and then allowed to cool to a glass. The glass is crushed into fine powder and loaded into a quartz sample tube. The tube is placed in a Ray-O-Net irradiation unit and subjected to UV irradiation at 254 nm for 20 to 30 minutes. The sample tube is then removed from the UV light and sealed for analysis. Degassing before and after the irradiation shows no effect on the EPR spectra. This method is a convenient way to produce matrix-isolated ionic radicals at room temperature. Their disordered state closely approximates the environment of similar compounds found in coal. Data on the model compounds is summarized in Table I [3].

We have used four microwave frequencies, S-band (2-4 GHz), X-band (9.5 GHz), Q-band (35 GHz), and W-band (95 GHz) to study the radicals produced by this method. CW saturation behavior of the organic radicals has been studied. Modulation amplitude profiles of the sample are routinely probed to achieve the best compromise between the S/N and resolution of possible hyperfine structure. Wide magnetic field scans have been performed for the sample at X-band to make sure all signals are accounted for. Low temperature experiments at liquid nitrogen temperature (77 K) were also performed for the sample at 9.5 GHz; no discernible difference in EPR parameters (g and linewidth) were observed, suggesting that the radical is a rigid structure at room temperature. Care has also been taken to avoid distortion of the signal by RC filters.

X-band and Q-band spectra were obtained from Varian E-line EPR spectrometers outfitted with a tracking Varian NMR gaussmeter and a HP frequency divider with a Fluke frequency counter. W-band EPR is performed using the spectrometer system built in our laboratory. All g-value measurements are based on direct field and frequency measurements. A statistical treatment of the g-matrix measured from seven independently prepared samples of DBT in BAG shows that experimental errors are very small (max. standard deviation, $\sigma_{g_{11}} = 11 \times 10^{-5}$). S-band ESEEM is done on a locally-built Electron Spin Echo (ESE) spectrometer.

A computer-assisted analysis using an EPR powder spectrum simulation program and the spectral parameter optimization routine based on the SIMPLEX algorithm are performed to: 1) confirm the direct measurements of principal g values, 2) extract possible hyperfine interaction, and 3) accurately assess the linewidths and lineshapes. The calculation of principal values of the g matrix is based on Stone's theory (ref Stone) with certain modifications. The SCF-MO wave function and orbital energies are obtained from the semi-empirical method PM3 in MOPAC (ref QCPE 455). All calculations employ an IBM R6000 workstation.

RESULTS AND DISCUSSION

The anisotropic g matrix is one of the most important and fundamental EPR parameters. It is generally viewed as characteristic of the electronic structure of the molecule that contains one or more unpaired electrons. But for most organic radicals, the elements of the g matrices are very close to the free-electron value ($g_0 = 2.00232$). Experimentally resolving such small differences was difficult using conventional 9.5 GHz EPR, and this greatly limited the usefulness of g matrix as a structure indicator. The development of very high frequency EPR (VHF-EPR) has overcome this problem. From the simple resonance condition one can see easily that the difference in resonance fields for two slightly different g factors is proportional to the product of the microwave frequency and the difference between the two g factors.

$$\Delta B = B_1 - B_2 = \frac{2\pi\hbar\nu}{\beta} \left(\frac{1}{g_2} - \frac{1}{g_1} \right) = (2\pi\hbar) \left(\frac{\Delta g}{g_1 g_2} \right) \nu$$

Therefore the g resolution will be enhanced by a factor of 10 on going from X-band (9.5 GHz) to W-band (95 GHz) providing the line does not broaden substantially with microwave frequency.

At a sufficiently high field, the electronic Zeeman interaction will dominate the electron-nuclear hyperfine interaction, and both the electron and nuclear spins will be quantized along the external field. Under favorable conditions, the anisotropic hyperfine coupling matrix, A, can be resolved or partially resolved along the canonical directions of g matrix, yielding additional valuable information about molecular structure and other properties related to the ground electronic state of a molecule. Indeed, we have observed the anisotropic A matrix in the continuous wave VHF-EPR spectra of a series of thiophenic radicals. In addition, an auxiliary experiment using a low frequency pulsed spectrometer at S-band (2-4 GHz) also reveals the anisotropic hyperfine interactions between the

electron spin and the ring protons.

The multifrequency approach has resulted in a unified set of magnetic parameters (g and A matrices), from which it is possible to identify and characterize the radical species in terms of properties related to its molecular orbital structure. The total spin energy Hamiltonian for an electron with spin S is written:

$$\mathcal{H}_{\text{spin}} = \mathcal{H}_{\text{ex}} + \mathcal{H}_{\text{so}} = \beta_e B \cdot (L + g_e S) + \lambda L \cdot S$$

The shift due to organic heteroatoms (O and S) results from a change in resonance energies caused by anisotropy in g_e and the spin-orbit constant λ , coupling the spin and orbital angular momenta (L). The larger the field shift ΔB , the more sensitive our experiment will be to the presence of sulfur. It is for this reason that we observed the shift due to sulfur at higher spectrometer frequencies. Since XANES results from Illinois coals shows that thiophenic sulfur is the aromatic form in which the majority of organic sulfur is found in these coals, the connection between molecular and electronic structure found in the series of model thiophenes can be used as a basis for the analysis of VHF-EPR spectra from coal.

Several experiments have been performed to test the accuracy of the VHF-EPR method for aromatic sulfur analysis in coal. The first of these tests was suggested by Dr. Ken Ho, ICCI project monitor, and consisted of making blends of two coals of known sulfur composition. VHF-EPR analyses of these blends then could be checked against the *known sulfur content*. Accordingly, a vitrinite (organic sulfur 2.9% dmf) and a sporinite (organic sulfur 4.25%) were blended, and the sulfur content of these blends measured by VHF-EPR was compared to the known composition. Figure 1 shows the results of this test. The VHF-EPR results agree with the known values to better than $\pm 0.1\%$.

The second type of test which was performed to evaluate the method was the direct analysis of organic sulfur content in a variety of coals of widely differing character, spanning the range of sulfur content from less than 0.5% to more than 11%. These coals were selected because each had been carefully analyzed for organic sulfur content by other chemical and physical methods. Figure 2 shows the excellent correlation between VHF-EPR analyses and the published organic sulfur content of these coals.

The third type of test which we performed to validate the VHF-EPR method was a direct comparison of results from the method and those obtained by XANES on identical samples. Sets of samples prepared by Dr. Steve Palmer, Southern Illinois University-Carbondale, were sent to Prof. G. Huffman, University of Kentucky, for analysis by XANES, as well as to us for analysis by VHF-EPR. Figure 3 shows the comparison of the two methods on four IBCSP coals. Nearly perfect agreement is seen in IBC 101, 102, and 106, while a considerable disagreement is seen in values for IBC 109. Figure 4 shows a similar comparison between VHF-EPR and IBCSP published values for *organic sulfur* in these coals. A comparison of Figures 3 and 4 shows that the VHF-EPR determination of aromatic sulfur is at variance with both XANES and proximate analytical data in the case of IBC 109, and that a much better correlation exists for the XANES data than for the proximate analytical data. The reasons for disagreement in the case of IBC 109 are currently being investigated.

CONCLUSIONS

This research and development project has demonstrated a new analytical method for determining the aromatic sulfur content of coals and coal-related materials. It is based on VHF-EPR technology, and is non-destructive, quick, and precise. The method requires only a few tenths of a milligram of sample. The precision of this measurement seems less sensitive to sample oxidation than does XANES, although a much more detailed comparison of the two methods clearly is in order. VHF-EPR analysis for aromatic sulfur seems a good choice for routine coal characterization. It also should be very useful in the evaluation of various desulfurization technologies, and as a monitor of the extent of desulfurization. Several scientific questions remain for future work. These include: (a) the effects of spin exchange in modifying observed g -values in coals; (b) the effects of oxygen and sample oxidation; and (c) the advantages of working at magnetic fields *higher than 3.4 T*. Additional instrument development and fundamental research on items (a) - (c) could extend the technique into the analysis of heteroatomic oxygen as well as sulfur.

This work was prepared with the support, in part by grants made possible by the Illinois Department of Energy and Natural Resources through its Coal Development Board and Illinois Clean Coal Institute (K. Ho, project manager), and by the U. S. Department of Energy (DE-FC22-92PC-92521). However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors, and do not necessarily reflect the views of IDENR, ICCI, and the DOE.

REFERENCES

1. "Electron Magnetic Resonance of Standard Coal Samples at Multiple Microwave Frequencies," R. B. Clarkson, W. Wang, D. L. Brown, H. C. Crookham, and R. L. Belford, in Techniques in Magnetic Resonance for Carbonaceous Solids, R. Botto and Y. Sanada, eds., ACS Advances in Chemistry Series 229, American Chemical Society, Washington, 1993, 507 - 528.
- "Multi-Frequency Electron Magnetic Resonance," R. L. Belford and R. B. Clarkson, in Techniques in Magnetic Resonance for Carbonaceous Solids, R. Botto and Y. Sanada, eds., ACS Advances in Chemistry Series 229, American Chemical Society, Washington, 1993, 107 - 138.
2. "Very High Frequency EPR - 94 GHz Instrument and Applications to Primary Reaction Centers from Photosynthetic Red Bacteria and Other Disordered Systems," W. Wang, R. L. Belford, R. B. Clarkson, P. H. Davis, J. Forrer, M. J. Nilges, M. D. Timken, T. Walczak, M. C. Thurnauer, J. R. Norris, A. L. Morris, and Y. Zhang, *Appl. Magn. Reson.*, **6**, 195 - 215 (1994).
3. "Electron Magnetic Resonance of Aromatic Radicals on Metal Oxide Surfaces," R. B. Clarkson, K. Mattson, W. Shi, W. Wang, and R. L. Belford, *Mol. Engineering*, **4**, 89 - 117 (1994).

Table I.
Summary of g-matrix values for selected thiophene radicals on alumina

Species	g_1	g_2	g_3
THI	2.00506±.00050	2.00506±.00050	2.00234±.00010
BTH	2.00642±.00038	2.00451±.00012	2.00226±.00013
DBT	2.01130±.00026	2.00624±.00015	2.00236±.00010
BNT	2.00583±.00012	2.00495±.00012	2.00224±.00011
DNT	2.00518±.00052	2.00326±.00047	2.00224±.00051

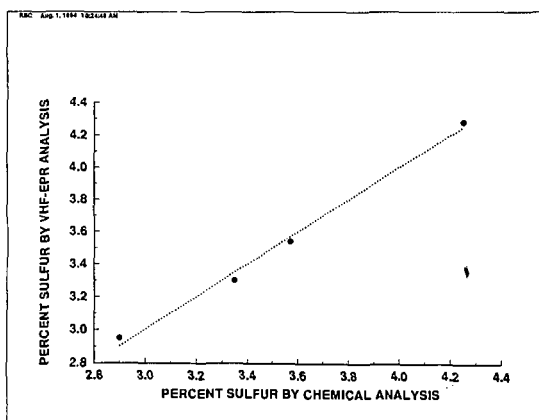


Figure 1. VHF-EPR sulfur analysis test on vitrinite/sporinite blends

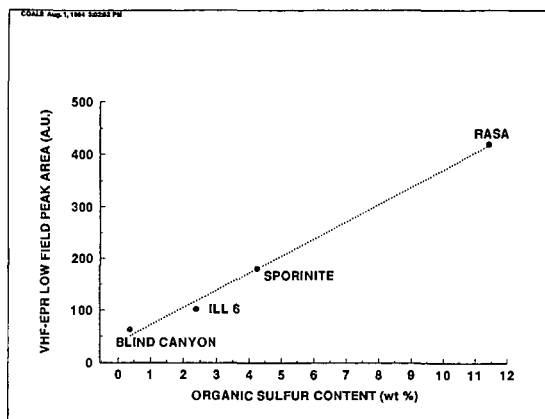


Figure 2. Correlation between VHF-EPR and other analytical methods for organic sulfur in a series of coals with widely differing sulfur contents.

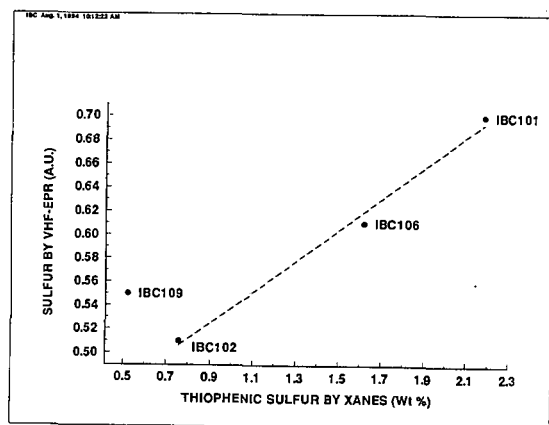


Figure 3. Comparison of VHF-EPR and XANES analyses on four IBCSP coals. The XANES figures are for thiophenic sulfur.

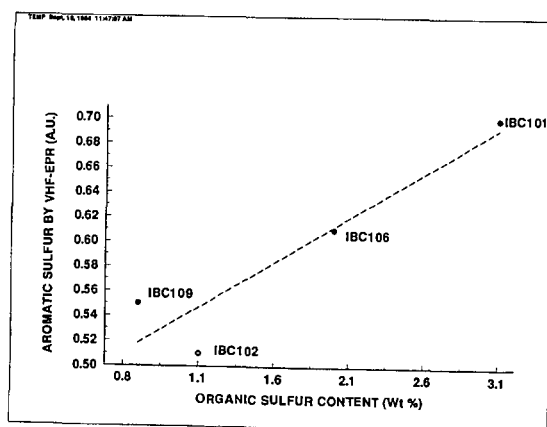


Figure 4. Comparison of VHF-EPR analytical results and IBCSP values for organic sulfur in four coals.